LARGE-SCALE MERCURY CONTROL TECHNOLOGY TESTING FOR LIGNITE-FIRED UTILITIES – OXIDATION SYSTEMS FOR WET FGD

Technical Progress Report

(For the period April 1 – June 30, 2006)

Prepared for:

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U.S. Department of Energy National Energy Technology Laboratory 626 Cochrans Mill Road PO Box 10940, MS 921-107 Pittsburgh, PA 15236-0940

DOE NETL Cooperative Agreement DE-FC26-03NT41991 EERC Funds 4318 and 4319 Performance Monitor: Andrew O'Palko

Prepared by:

Steven A. Benson Michael J. Holmes Kevin C. Galbreath Donald P. McCollor Jill M. Mackenzie Lingbu Kong Charlene R. Crocker

Energy & Environmental Research Center University of North Dakota 15 North 23rd Street, Stop 9018 Grand Forks, ND 58202-9018

> Carl Richardson Katherine Dombrowski

URS Corporation 9400 Amberglen Boulevard Austin, TX 78729

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Prepared for:

Ms. Karlene Fine

North Dakota Industrial Commission State Capitol, 10th Floor 600 East Boulevard Avenue Bismarck, ND 58505-0310

NDIC Agreement No. FY-L-125 EERC Fund 4927

Prepared by:

Steven A. Benson Michael J. Holmes Kevin C. Galbreath Donald P. McCollor Jill M. Mackenzie Lingbu Kong Charlene R. Crocker

Energy & Environmental Research Center University of North Dakota 15 North 23rd Street, Stop 9018 Grand Forks, ND 58202-9018

> Carl Richardson Katherine Dombrowski

URS Corporation 9400 Amberglen Boulevard Austin, TX 78729

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ABBREVIATIONS

AA atomic absorption

ASTM American Society for Testing and Materials

CCB coal combustion by-product
DMA direct mercury analyzer
ESP electrostatic precipitator
LTL long-term leaching

SGLP synthetic groundwater leaching procedure TCLP toxicity characteristic leaching procedure

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LARGE-SCALE MERCURY CONTROL TECHNOLOGY TESTING FOR LIGNITE-FIRED UTILITIES – OXIDATION SYSTEMS FOR WET FGD

MERCURY STABILITY ANALYSIS OF MILTON R. YOUNG UNIT 2 COAL COMBUSTION BY-PRODUCTS

Background

The mercury emission control technologies being developed to remove mercury from flue gases are in many cases designed to incorporate the mercury removed from flue gas into the fly ash or flue gas desulfurization (FGD) material. Significant changes in the chemical composition, physical properties, and morphology of coal combustion by-products (CCBs) may occur as a result of the application of new emission controls. The stability of mercury associated with CCBs is currently under investigation at the Energy & Environmental Research Center (EERC). The reasons for evaluating the rerelease of mercury from CCBs are twofold: 1) to determine if mercury captured on CCBs is stable or if it will be rereleased from these materials, thus negating the purpose of the removal of the mercury from the emissions, and 2) to aid utilities in determining and understanding changes in CCBs associated with mercury control and associated CCB management.

The rerelease mechanisms for mercury from CCBs have been identified as 1) direct leachability, 2) vapor-phase release at ambient and elevated temperatures, and 3) biologically induced leachability and vapor-phase release. Leaching is the most likely mechanism of transport of constituents from disposed or utilized CCBs contacted by water. Leaching is typically performed on CCBs to characterize them for management purposes. Several issues have been raised by the U.S. Environmental Protection Agency's (EPA's) Office of Research and Development and Office of Solid Waste related to the best means of evaluating the leaching potential of CCBs. Vapor-phase release, particularly of mercury, is important from the perspective of long-term use, storage, or disposal of CCBs. Although the concentration of mercury in CCBs is relatively low, the large volumes of CCBs produced annually cause concern about potential mercury releases. Ambient- and elevated-temperature studies of mercury release resulted in the development of equipment to determine mercury release in real time from CCBs. EERC results are presented regarding mercury release from CCBs subjected to laboratory tests designed to simulate the identified release mechanisms.

Project Overview

Mercury Stability in By-Products

This task is focused on the evaluation of fly ash collected from electrostatic precipitator (ESP) hoppers from baseline and mercury control technology testing conditions. Experiments conducted were designed to assess the potential for rerelease of mercury from these fly ashes under different controlled laboratory conditions similar to those that CCBs might be exposed to in disposal and utilization environments.

Leaching

Leaching is the most likely mechanism of transport of constituents from disposed or utilized CCBs contacted by water. Leaching is typically performed on CCBs to characterize them for management purposes. The leaching procedure used for these samples was the synthetic groundwater leaching procedure (SGLP) with long-term leaching (LTL) (Hassett, 1998). The long-term component is utilized on reactive CCBs.

The SGLP batch leaching procedure is a relatively simple test that follows many of the conditions of the toxicity characteristic leaching procedure (TCLP) (EPA, 1997) and ASTM International D3987 (ASTM, 1989). The test utilizes a 20:1 liquid-to-solid ratio, end-over-end agitation at approximately 30 rpm, an 18-hour equilibration time, and usually employs a leaching solution consisting of water from the site, water that has been prepared in the lab similar to water likely to contact the ash, or distilled deionized water. Distilled deionized water was used in this effort. For the long-term component of this procedure, multiple bottles are set up and analyzed at different time intervals. A typical SGLP and LTL test consisting of 18-hour, 30-day, and 60-day equilibration times was performed in this effort. Although 60 days is often not long enough to have achieved complete equilibrium, it is generally long enough to determine the concentration evolution of individual parameters. The most important factor when performing LTL is to have at least three equilibration times to determine a true trend.

Leachates were filtered through 0.45-µm filter paper and analyzed for total mercury. Mercury leachate concentrations were determined using a cold vapor atomic absorption (AA) technique.

Thermal Stability

A schematic for the controlled thermal desorption of mercury and mercury compounds was assembled and is shown schematically in Figure 1. The apparatus was constructed using an AA spectrophotometer for mercury detection and included a small tube furnace and temperature controller for thermal desorption. A Hewlett Packard 3395 integrator was used for data collection. Detection of thermally desorbed mercury and mercury compounds was done in an electrically heated quartz cell operated at 800°C. The use of a heated cell allowed detection of mercury compounds by thermally decomposing compounds to form elemental mercury, which can be detected by AA. Nitrogen gas flow was maintained at 5 cm³/min through the AA. The temperature controller was ramped from ambient temperature to 750°C at a rate of 25°C per minute.

Results

Mercury Stability Analysis

Fly ash samples were collected from the ESP hoppers for use in this evaluation. Sample 05-005 was collected on March 17, 2005, under pre-mercury control (baseline) conditions.

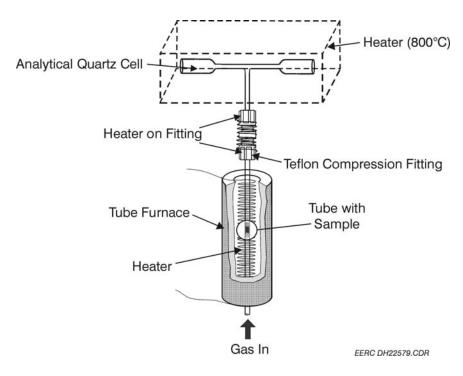


Figure 1. Mercury thermal desorption apparatus.

Sample 05-017 was collected on April 13, 2005, during mercury control technology testing with activated carbon and SEA2 injection.

Before leaching and thermal stability experiments were performed, the total mercury content and pH of the solid samples were determined, and the results are reported in Table 1. Total mercury content was determined using a DMA-80 (direct mercury analyzer). The total mercury content is higher in the fly ash sample collected during mercury control testing than the baseline sample. The pH of samples was determined using distilled water after 24 hours of stirring. A pH >10 indicated that LTL should be applied in order to assess the impact of reactivity of the material on the leaching profile of the sample. CCBs exhibiting a high pH have the potential to undergo hydration reactions that can change the leaching profile with time.

Leaching

Leaching data, consisting of final leachate pH and mercury concentrations, on the CCB samples using SGLP and 30- and 60-day LTL tests are shown in Table 2. Duplicate 60-day LTL

Table 1. Fly Ash Characterization

ID No.	Mercury Control	Total Mercury, μg/g	Initial pH	24-hr pH	
05-005	None	0.431	11.77	11.57	
	Activated carbon and SEA2				
05-017	injection	0.717	12.04	11.77	

Table 2. Leaching Data on Fly Ash Samples

		Leaching	Mercury,	Leachate
ID No.	Mercury Control	Procedure	μg/L	pН
05-005	None	SGLP	< 0.01	11.73
05-005	None	30-day LTL	< 0.01	11.61
05-005	None	60-day LTL	< 0.01	11.84
05-005	None	60-day LTL	< 0.01	11.83
05-017	Activated carbon and SEA2 injection	SGLP	< 0.01	11.94
05-017	Activated carbon and SEA2 injection	30-day LTL	< 0.01	11.69
05-017	Activated carbon and SEA2 injection	60-day LTL	< 0.01	12.01
05-017	Activated carbon and SEA2 injection	60-day LTL	< 0.01	11.99

was performed yielding reproducible leachate mercury values. All leachates gave results below the reporting limit.

Thermal Stability

The generation of mercury thermal desorption curves for the two samples was technically challenging. Sample 05-005 was tested as received and after sample modification. The sample was run through a 100-mesh sieve when what appeared to be black chunks were discovered in the sample. The sieved sample was then tested. Sample 05-017 was tested as received.

An example of the mercury thermal desorption curve generated on the AA for Sample 05-005 is shown in Figure 2 and for sample 05-017 in Figure 3. Both samples generally desorbed mercury at one peak temperature. However, Sample 05-017 occasionally produced an additional minor peak above 550°C. The average mercury release peak temperatures for the samples are given in Table 3, which includes a separation of the unmodified and modified Sample 05-005. The data in Table 3 reveal several points about the two samples. The mercury evolved from Sample 05-005 at a lower temperature in the modified sample than in the unmodified sample. Therefore, the particles that did not pass through a 100-mesh sieve appeared to retain or interact with the mercury present on the other particles. When comparing Samples 05-005 and 05-017, it is evident that the activated carbon and SEA2 injection changed the mercury present on the fly ash or the mechanism of mercury release.

Both samples had low recovery rates. Upon further examination, it was found that a mercury compound was depositing on the cool area of the tube (~200°C) prior to detection by the AA. The samples were tested on the DMA for any remaining mercury after a select number of runs on the AA. No mercury was detected on Sample 05-005; however, a minute amount was detected on Sample 05-017.

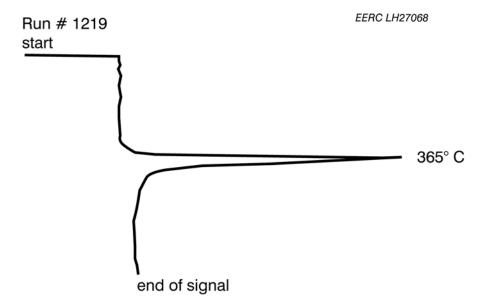


Figure 2. Sample 05-005 example AA mercury thermal desorption curve.

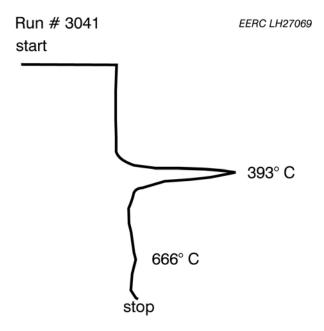


Figure 3. Sample 05-017 example AA mercury thermal desorption curve.

Table 3. Average Mercury Thermal Desorption Peak

				% Relative	
		Average	Standard	Standard	Number of
Sample	Mercury Control	Peak, °C	Deviation	Deviation	Runs
05-005, All Runs	None	353	30.4	8.6%	7
05-005, Unmodified	None	375	9.6	2.6%	3
05-005, Modified	None	336	29.8	8.9%	4
05-017	Activated Carbon				
	and SEA2				
	Injection	402	8.8	2.2%	7

Discussion of Implication of Results

Mercury Stability in CCBs

Leaching

Results of leaching of the CCB samples show no detectible mercury release.

Thermal Stability

Generally speaking, most CCBs exhibit a single- or double-peak mercury release profile. Mercury is released at temperatures greater than 200°C, and in many samples, all the mercury is released when exposed to a temperature of 750°C (Hassett et al., 2005). The fly ash samples collected under baseline (Sample 05-005) and mercury control technology testing conditions (Sample 05-017) at the Milton R. Young power plant showed mercury release peaks at greater than 320°C, with Sample 05-017 releasing the primary mercury peak at approximately 400°C. Sample 05-017 also occasionally exhibited additional mercury release above 550°C and retained a minimal amount of mercury on the sample after heating to 750°C. It is evident from the thermal stability testing performed that activated carbon and SEA2 injection changed the mercury present on the fly ash or the mechanism of mercury release.

ADDITIONAL ACTIVITIES: THE MEGA SYMPOSIUM

The paper entitled "Large-Scale Mercury Control Technology Testing for Lignite-Fired Utilities – Oxidation Systems for Wet FGD" in Appendix A was prepared this quarter. It will be presented by Mr. Kevin Galbreath at *The Mega Symposium* in Baltimore, Maryland, in Session 2: Mercury: Oxidation Technologies, on August 29, 2006, at 10:05 a.m. in the Baltimore Marriott Waterfront.

REFERENCES

- ASTM International. *Standard Method for Shake Extraction of Solid Waste with Water*. In Annual Book of ASTM Standards; Section 11: Water and Environmental Technology, ASTM D3987-85, 1989.
- Hassett, D.J. Synthetic Groundwater Leaching Procedure, Encyclopedia of Environmental Analysis and Remediation. pp. 4797–4803, John Wiley & Sons, Inc., 1998.
- Hassett, D.J.; Heebink, L.V.; Pflughoeft-Hassett, D.F.; Zacher, E.J.; Buckley, T.D.; Eylands, K.E. Mercury and Air Toxic Element Impacts of Coal Combustion By-Product Disposal and Utilization; Final Year 2 Annual Report for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-02NT41727; EERC Publication 2005-EERC-06-09; Energy & Environmental Research Center: Grand Forks, ND, Jun 2005.
- U.S. Environmental Protection Agency Method 1311, *Toxicity Characteristic Leaching Procedure, Test Methods for Evaluating Solid Waste*, Physical/Chemical Methods, EPA Publication SW-846, Third Edition, as amended by Updates I, II, IIB, and III, finalized in the Federal Register on June 13, 1997.

APPENDIX A PAPER FOR THE MEGA SYMPOSIUM

Large-Scale Mercury Control Technology Testing for Lignite-Fired Utilities – Oxidation Systems for Wet FGD

Donald P. McCollor¹, Steven A. Benson¹, Michael J. Holmes¹, Stuart Libby², Jill M. Mackenzie¹, Charlene R. Crocker¹, Lingbu Kong¹, and Kevin C. Galbreath¹

¹University of North Dakota Energy & Environmental Research Center, 15 North 23rd Street, Stop 9018, Grand Forks, ND 58202-9018

²Minnkota Power Cooperative, Inc., 1822 Mill Road, Grand Forks, ND 58208-3200

Paper No. 9

ABSTRACT

Mercury (Hg) control technologies were evaluated at Minnkota Power Cooperative's Milton R. Young (MRY) Station Unit 2, a 450-MW lignite-fired cyclone unit near Center, North Dakota. A cold-side electrostatic precipitator (ESP) and wet flue gas desulfurization (FGD) are used at MRY for controlling particulate and sulfur dioxide (SO₂) emissions, respectively. Calcium chloride (CaCl₂), magnesium chloride (MgCl₂), and a proprietary sorbent enhancement additive (SEA), hereafter referred to as SEA2, were added to the coal feed to enhance Hg capture in the ESP and/or wet FGD. In addition, powdered activated carbon (PAC) was injected upstream of the ESP. Preliminary baseline analyses indicated that total Hg concentrations at the ESP and wet FGD inlets varied from about 12 to 16 µg/Nm³, whereas at the stack concentrations were consistently at about 13 ug/Nm³. The ESP and wet FGD were very inefficient at removing Hg. primarily because Hg⁰ was dominant. MgCl₂ and CaCl₂ were relatively ineffective in promoting Hg⁰ oxidation and capture in the ESP-wet FGD. Relatively low additions of SEA2, however, significantly improved the Hg removal efficiency of the ESP-wet FGD, although the goal of 55% Hg removal was not achieved using as much as 75 ppm SEA2 (dry coal basis). Most of the Hg removal occurred in the ESP, suggesting that SEA2 addition promoted the conversion of Hg⁰ to particulate bound Hg. SEA2 addition combined with 0.15-lb/Macf PAC injection was performed for a month during which Hg removals ranged from 50% to 65%.

INTRODUCTION

The Energy & Environmental Research Center (EERC) is leading a consortium involving ADA-ES, Babcock & Wilcox Company (B&W), the U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL), Electric Power Research Institute (EPRI), the North Dakota Industrial Commission, and SaskPower, as well as a Mercury Task Force consisting of Basin Electric Power Cooperative; BNI Coal, Ltd.; Dakota Westmoreland Corporation; Great River Energy; Minnkota Power Cooperative, Inc. (MPC); Montana–Dakota Utilities Co.; North American Coal Corporation; Otter Tail Power Company; and TXU Energy (TXU) to evaluate cost-effective approaches for capturing the mercury (Hg) occurring in lignitic combustion flue gases using a cold-side electrostatic precipitator (ESP) and/or wet flue gas desulfurization (FGD) system. This project was developed in response to the U.S. Environmental Protection Agency

(EPA) decision to regulate Hg from utility power plants and a DOE solicitation requesting additional information on the performance of Hg control technologies for lignite-fired utilities. U.S. power plants burning lignite generally release greater proportions of elemental mercury (Hg⁰) than those burning bituminous coals. Hg⁰ is the most difficult chemical species of Hg to remove from flue gas and, therefore, requires an innovative Hg control approach (1).

The overall project goal was to cost-effectively oxidize most of the Hg^0 in lignitic combustion flue gases into a more soluble and reactive inorganic mercuric compound (Hg^{2^+}) that could subsequently be captured in an ESP and/or wet FGD system. Hg^0 oxidation processes have been demonstrated using pilot-scale and short-term full-scale tests (2–4). Longer-term full-scale testing is required to further demonstrate and optimize Hg^0 oxidation technologies. The applicability of this Hg control approach is expected to increase with the demand for wet FGD systems in lignite and subbituminous coal-fired power plants in the United States and Canada.

MPC's Milton R. Young (MRY) Station Unit 2 near Center, North Dakota, was one of two host sites for field testing as part of the project entitled Large-Scale Mercury Control Technology Testing for Lignite-Fired Utilities – Oxidation Systems for Wet FGD. The other site was TXU Monticello Steam Electric Station (MoSES) Unit 3 near Mt. Pleasant, Texas. An ESP and wet FGD are used at MRY for controlling particulate and sulfur dioxide (SO₂) emissions, respectively. Hg removal technologies investigated at MRY were Hg⁰ oxidizing agents, sorbent enhancement addition (SEA), and powdered activated carbon (PAC) injection. Calcium chloride (CaCl₂), magnesium chloride (MgCl₂), and a proprietary SEA, hereafter referred to as SEA2, were added to the coal feed to enhance Hg capture in the ESP and/or wet FGD. The PAC injected at MRY Unit 2 was NORIT Americas Inc. DARCO® Hg, a lignite-based activated carbon manufactured specifically for the removal of Hg in coal-fired utility flue gas streams. The EERC collaborated with B&W, EPRI, URS, and ADA-ES in performing the technical work on this project, involving Hg measurements upstream and downstream of ESP and wet FGD units before and during CaCl₂, MgCl₂, and SEA2 additions and PAC injections; determining the Hg removal efficiencies of ESP and wet FGD units; quantifying the balance-of-plant impacts of the control technologies; and facilitating technology commercialization.

EXPERIMENTAL

Description of MRY Unit 2

MRY is owned and operated by MPC, with headquarters in Grand Forks, North Dakota, and a subsidiary, Square Butte Electric Cooperative. MRY is in Oliver County in western North Dakota's coal country, about five miles east, and three miles south of Center, North Dakota. MRY Unit 2 is a B&W Carolina-type radiant boiler designed to burn North Dakota lignite. Nominally rated at 3,050,000 lb/hr, this unit is a cyclone-fired, balanced-draft, pump-assisted circulation boiler. The unit began commercial operation in May 1977 and is base-loaded at 450 MW gross. A cold-side ESP with a specific collection area of 375 ft²/kacfm and spray tower FGD system utilizing alkaline ash and lime are used for particulate and SO₂ control, respectively. General information on the lignite coal burned at MRY is presented in Table 1.

Table 1. Coal information for Milton R. Young Station

Owner and Operator	Mine	Seam Mined	Location	Mine Production, ^a tons
BNI Coal, Ltd. a wholly owned subsidiary of Allette	Center	Kinneman Creek and Hagel	Western, northern lignite basin, North Dakota	4,522,831

^a Keystone Coal Industry Manual; Mining Media: Prairieville, LA, 2004.

A schematic of MRY Unit 2 showing sampling and fuel addition locations is provided in Figure 1. From October 22 through November 14, 2002, the Hg emission and control characteristics of the MRY Unit 2 were evaluated at the ESP inlet, wet FGD inlet, and stack using the Ontario Hydro (OH) method and continuous mercury monitors (CMMs) (5). Statistical analyses of the CMM data indicated that the average total Hg concentration was $10.7 \pm 2.7 \, \mu g/m^3$ (90th percentile) at the wet FGD inlet and $9.3 \pm 2.2 \, \mu g/m^3$ at the stack. The average total Hg stack emissions were composed of 95% Hg⁰. Fluctuations in total Hg concentrations resulting from coal heterogeneity and variability in plant operations were within 24% of the average values. Hg mass balances for MRY Unit 2 ranged from 102% to 103% (1, 5).

Chemical Addition System

The aqueous $CaCl_2$, $MgCl_2$, and SEA2 addition system consisted of three 3100-gal storage tanks, a metering and pumping skid, and injection lances. The system pumped solutions at rates of 0.1 to 2.2 gal/min corresponding to concentrations of ≤ 500 ppm on an as-fired coal basis. The solutions were injected into the coal pipes feeding four of the 12 Unit 2 cyclones.

Fuel Air Economizer Coal Additive Electrostatic Preheater (oxidant) Boiler Scrubber Precipitator Towers Hoppers Hoppers Stack Ash Sluice Hoppers Water from Nelson Lake Silo Fly Ash Lime Ash Sluice Slurry Tank Bottom Ash Lime Settling Tank Preparation Slurry Blowdown ······ Solids Solids --- Gases (slag, ash) FGD Pond Return Liquids FGD Sludge Pond Sample Location EERC SB21575.CDR

Figure 1: Schematic of MRY Unit 2 showing sampling and coal additive locations.

PAC Injection System

A PAC injection system was supplied and installed by Apogee upstream of the ESP. The PAC injection system consisted of an Apogee Portapac metering skid, blower, connecting lines, and injection lances. The Portapac system includes provision for loading 900-lb supersacks of PAC, along with a discharge hopper, feed screw, blower, eductor, and discharge hose. PAC was injected using four lances in each of the four ESP inlet ducts. PAC consumption was approximately a 900-lb supersack every two days.

Hg Control Test Matrix

Presented in Table 2 is a schedule of test conditions, chemical additions, and PAC injections that were performed at MRY Unit 2 from mid-March to mid-May of 2005. Baseline testing was performed to characterize the inherent Hg emission characteristics of MRY Unit 2 during routine power plant operations. Parametric testing was performed to identify the chemical additions and PAC injections required to achieve the targeted ESP—wet FGD Hg removal efficiency of 55%. Early in the long-term testing, it was determined that the SEA2 addition rate required to achieve the Hg removal goal was untenable, and therefore a small amount of PAC was injected at the ESP inlet to further enhance Hg removal.

Table 2. Schedule of test conditions, chemical additions, and PAC injections performed at MRY Unit 2.

Week	Date	Test Condition	Chemical Additions, ppm ¹	PAC Injection
1	March 2005	Baseline	NA^2	NA
2–3	April 2005	Parametric	CaCl ₂ , MgCl ₂ , and SEA2, 25– 500	0.2–3.6 lb/min
4–11	April–May 2005	Long-term	SEA2, 60–100	0.15 lb/min

¹Dry coal basis.

Mercury Monitoring

CMMs, Tekran Model 2537A atomic fluorescence-based Hg vapor analyzers in conjunction with PS Analytical S235C400 wet-chemistry conversion units, were used to continuously monitor Hg⁰ and total Hg concentrations at the wet FGD inlet and stack locations. The PS Analytical uses two separate liquid flow paths, one to continuously reduce Hg²⁺ to Hg⁰, resulting in a total gas-phase Hg sample, and the other to continuously scrub out Hg²⁺, resulting in an Hg⁰ sample. The PS Analytical also uses a Peltier thermoelectric cooler module to cool and dry the sample gases prior to analysis. Additional Hg measurements were performed using the ASTM International Method D6784-02 (Standard Test Method for Elemental, Oxidized, Particle-Bound, and Total Mercury in Flue Gas Generated from Coal-Fired Stationary Sources), commonly referred to as the OH method, to provide Hg speciation results and to verify measurements obtained with the CMMs.

²Not applicable.

RESULTS AND DISCUSSION

BASELINE HG EMISSION CHARACTERISTICS

OH Hg measurements were performed in triplicate to quantify baseline Hg species concentrations at the ESP and wet FGD inlets and stack prior to any chemical additions or PAC injections. The average baseline Hg speciation measurement results are presented in Figure 2. Total Hg concentrations at the ESP and wet FGD inlets varied from about 12 to 16 µg/Nm³, whereas at the stack, concentrations were consistently at about 13 µg/Nm³, indicating that the ESP and wet FGD were very inefficient at removing Hg. The Hg speciation results in Figure 2 are very similar to those obtained in 2002 (1, 5). In both cases, Hg(p) concentrations were significant at the ESP inlet probably because of a known measurement bias associated with the OH sampling of Hg in the presence of relatively high fly ash concentrations. The results obtained at the wet FGD inlet and stack that indicate Hg⁰ as the most abundant species are probably more representative of the actual flue gas Hg speciation.

Parametric Hg Control Technology Testing

Parametric testing at MRY Unit 2 was performed using $CaCl_2$, $MgCl_2$, and SEA2 at varying addition rates alone and in combination with PAC injections to determine the most effective conditions for achieving ESP–wet FGD Hg removal efficiencies of $\geq 55\%$.

Plotted in Figure 3 are ESP–wet FGD Hg removal efficiencies as functions of MgCl₂, CaCl₂, and SEA2 addition rates. MgCl₂ and CaCl₂ were relatively ineffective in promoting Hg⁰ oxidation and capture in the ESP–wet FGD. Relatively low additions of SEA2, however, significantly improved the Hg removal efficiency of the ESP–wet FGD, although the goal of 55% Hg removal was not achieved using as much as 75 ppm SEA2. Nearly all of the Hg removal occurred in the ESP, suggesting that SEA2 addition promoted the conversion of Hg⁰ to Hg(p) which was subsequently captured in the ESP.

A combination of PAC injection and SEA2 addition provided the best Hg capture, much better than that observed with SEA2 addition alone (Figure 3). As indicated by the OH measurment results in Figure 4, nearly all of the Hg removal during PAC injection and SEA2 additions occurred in the ESP and primarily Hg⁰ exited the ESP, and wet FGD. Hg removals of \geq 50% were attained with 50 ppm SEA2 addition and 0.3–0.5 lb/Macf PAC injection.

Figure 2: Preliminary triplicate (A, B, and C) OH Hg species measurement results obtained during baseline MRY Unit 2 Hg control testing.

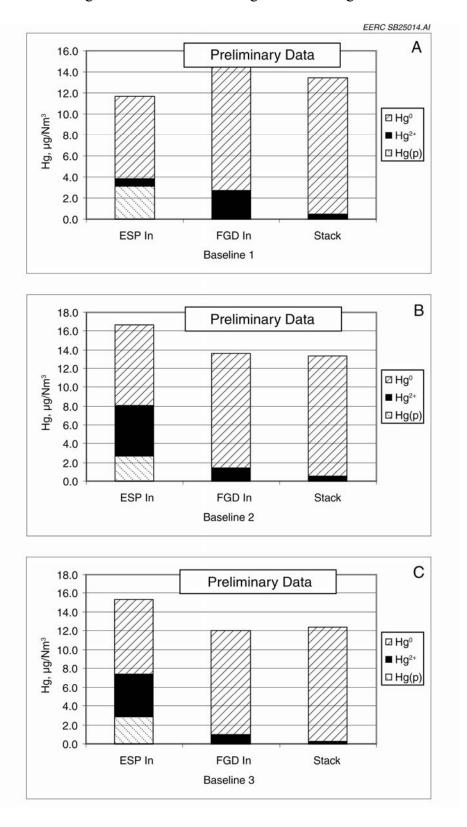
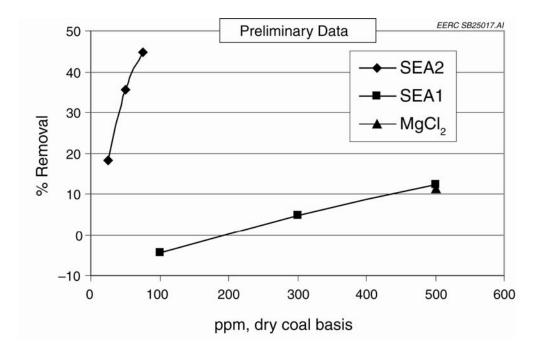


Figure 3: Preliminary ESP-wet FGD Hg removal efficiencies during CaCl₂, MgCl₂, and SEA2 additions.



Long-Term Hg Control Technology Testing

The objective of the relatively long-term testing at MRY Unit 2 was to demonstrate that approximately 55% Hg removal could be maintained for a month. The ESP–wet FGD Hg removal efficiencies are presented in Figure 5. Initially, Hg removals as high as 75% were attained but only at relatively high SEA2 injection rates of >100 ppm (dry coal basis). Relatively high SEA2 addition rates combined with 0.15 lb/Macf of PAC injection were required to consistently meet the 55% Hg removal goal. Injection of SEA2 in combination with a nominal 0.15-lb/Macf PAC injection was initiated on April 19 and continued until May 18, 2005. PAC injection continued for several hours on May 19 in the absence of SEA2 addition. During SEA2 addition and PAC injection, Hg removal efficiencies generally ranged from 50% to 65%.

CONCLUSIONS

The ESP and wet FGD at MRY Unit 2 were very inefficient at removing Hg from the lignite coal combustion flue gas, primarily because Hg⁰ was dominant. MgCl₂ and CaCl₂ were relatively ineffective in promoting Hg⁰ oxidation and capture in an ESP–wet FGD. Relatively low additions of SEA2, however, significantly improved the Hg removal efficiency of the ESP–wet FGD, although the goal of 55% Hg removal was not achieved using as much as 75 ppm SEA2 (dry coal basis). Most of the Hg removal occurred in the ESP suggesting that SEA2 addition promoted the conversion of Hg⁰ to particulate bound Hg. SEA2 addition combined with 0.15-lb/Macf PAC injection was performed for a month during which Hg removal efficiencies generally ranged from 50% to 65%.

Figure 4: OH Hg speciation results obtained during PAC injection at 0.25 lb/Macf and SEA2 additions at A) 25 ppm and B) 50 ppm (on a dry coal basis).

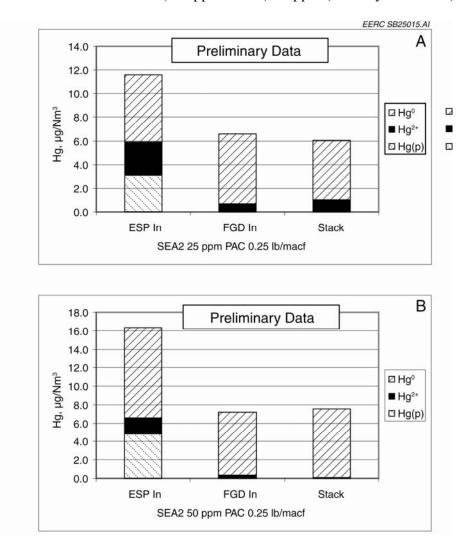
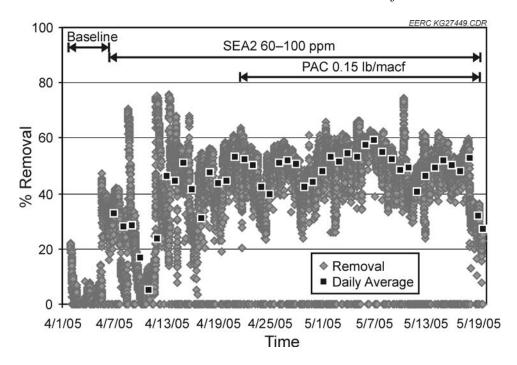


Figure 5: ESP-wet FGD Hg removal efficiencies during long-term testing at MRY Unit 2 using SEA2 additions and SEA2 addition with PAC injection.



DISCLAIMER

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REFERENCES

- 1. Pavlish, J.H.; Holmes, M.J. Mercury Control for Lignite-Fired Power Plants Poses Challenge. *Center for Air Toxic Metals Newsletter* **2002**, 8 (1), 6.
- 2. Pavlish, J.H.; Sondreal, E.A.; Mann, M.D.; Olson, E.S.; Galbreath, K.C.; Laudal, D.L.; Benson, S.A. Status Review of Mercury Control Options for Coal-Fired Power Plants. *Fuel Process. Technol.* **2003**, 82 (2, 3), 89–165.

- 3. Sjostrom, S.; Richardson, C.; Chang, R. *Evaluation of Mercury Emissions and Control Options for Great River Energy*; Final Report for North Dakota Industrial Commission; June 2001.
- 4. Chang, R.; Strohfus, M. *The Evaluation of Chemical Additives for Mercury Emission Control at Great River Energy*; Final Report for the North Dakota Industrial Commission; Jan 2003.
- 5. Thompson, J.S.; Holmes, M.J.; Laudal, D.L. *Long-Term Monitoring at North Dakota Power Plants*; Final Report for the North Dakota Industrial Commission; March 2003.

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A.	AWARDEE ACTION (AWARDEE COMPLETES PART A. 1-5	
1.	=	esting for Lignite-Fired Utilities – Oxidation Systems
2. Oth	for Wet FGD Type of Document: ■ Technical Progress Report □ □ Abstract □ Technical Paper □ Jour her (please specify)	nal Article Conference Presentation
3.	Date Clearance Needed:	
4 4.	Results of Review for Possible Inventive Subject Matter:	
	a. No Subject Invention is believed to be disclosed therei	n.
	b. ☐ Describes a possible Subject Invention relating to	
	i. Awardee Docket No.:	
	ii. A disclosure of the invention was submitted on	
	iii. A disclosure of the invention will be submitted by the follower	lowing date:
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	☐ will be applied for by the following date:	
♦ 5.	Signed	Date
	(Awardee)	
	ne & Phone No. <u>Sheryl E. Landis (701) 777-5124</u> ress Energy & Environmental Research Center, 15 North 23rd \$	
Addit	Tess Ellergy & Elivironmental Research Center, 15 North 2510 C	Street, Stop 90 to, Grand Forks, ND, 36202-90 to
В.	DOE PATENT COUNSEL ACTION	
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Mercury Control Technology Phase II Field Testing "Large-Scale Mercury Control Technology Testing for Lignite-Fired Utilities – Oxidation Systems for Wet FGD"



Project Summary
DE-FC26-O3NT41991

Last Updated: June 30, 2006

National Energy Technology Laboratory





Project Objectives

- Determine the impact of chemical addition on mercury speciation and overall mercury removal from flue gas using the combination of an electrostatic precipitator and a wet scrubber.
- Test the mercury removal technology for a full-scale North Dakota lignite-fired unit at Minnkota Power's Milton R. Young (MRY) Unit 2.
- Test the mercury removal technology for a full-scale Texas lignitefired unit at TXU's Monticello Unit 3.
- Measure baseline mercury speciation and removal.
- Measure mercury speciation and removal with the control technology.
- Evaluate variability of mercury removal and emissions while applying the control technology.
- Determine the balance-of-plant effects as a result of using the control technology.
- Perform a preliminary economic evaluation.



Partnership Team









North Dakota Industrial Commission





























Project Principals

- Project Manager: Steven Benson, Energy & Environmental Research Center (EERC), sbenson@undeerc.org, (701) 777-5177
- Denny McDonald, Babcock & Wilcox Company
- Stu Libby, Minnkota Power Cooperative
- Bob Weimuth, TXU Energy
- Ramsay Chang, Electric Power Research Institute
- Carl Richardson, URS Corporation
- Project Manager: Andrew O'Palko, U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL)



Budget

Start Date	End Date	Government Cost	Performer Cost	Total Cost	Cost Share
9/26/03	9/25/06	\$1,602,195 Proposed	\$536,335 Proposed	\$2,138,530 Proposed	25.1%
9/26/03	9/25/06	\$1,602,195 Obligated	\$536,335 Obligated	\$2,052,915 Obligated	Obligated

• DOE Costs to Date: \$1,217,500.82

• Cost Share to Date: \$197,687.70



Highlights of Progress to Date

- Contract negotiated with DOE.
- Site visit by the EERC and Babcock & Wilcox to MRY, December 11, 2003.
- Site visit by URS to Monticello, February 2004.
- Completed hardware design, procurement, and fabrication of hardware common to MRY, Leland Olds, and Antelope Valley Stations under program DE-FC26-03NT41991.
- Installed corrosion probes for baseline testing at MRY which will be removed in early January 2005.
- Completed test plan for MRY.
- Installed sorbent enhancement additive (SEA) skid, powdered activated carbon (PAC) injection system, and sampling ports at MRY.
- Removed baseline corrosion probes and replaced them with probes to be exposed during the 4-week test period at MRY.



Highlights of Progress to Date (Cont.)

- Mercury sampling and measuring equipment was brought on-site and installed at MRY.
- Two trailers for on-site analysis, coordination of sampling activities, and preparation of sampling trains were brought on-site at MRY.
- Completed baseline and parametric testing at MRY.
- Completed longer-term testing of SEA and SEA with PAC at MRY.
- Met with URS to discuss results of MRY and possible implications related to application of oxidation technologies to Monticello.
- Completed testing of oxidation technologies for Hg control at MRY and attained about 55% removal
- Sight visits and testing initiated at Monticello.
- Completed testing at Monticello.
- Completed mercury stability testing for MRY.



Project Tasks and Status

Task	Description	Status
1	Pretest activities, MRY Station	Site visit completed 12/11/04
2	Testing, MRY	Parametric testing completed March 31, 2005; long-term testing completed May 19, 2005.
3	Data reduction and reporting, MRY	In progress
4	Pretest activities, Monticello	Site visit completed 02/04. Draft test plan sent out March 30.
5	Testing, Monticello	Parametric testing occurred on October 27–30, 2005; long-term testing completed December 14, 2005.
6	Data reduction and reporting, Monticello	In progress
7	Final report	In progress



Project Milestones

Milestone	Description	Status
1	Negotiate and award contract	Completed
2	Kickoff meeting	Completed
3	Site visit, MRY	Completed
4	Site visit, Monticello	Completed
5	Test plan, MRY	Completed
6	Test plan, Monticello	Completed
7	Quality assurance/quality control (QA/QC) plan, MRY	Completed
8	QA/QC plan, Monticello	Completed
9	Testing, MRY	Completed
10	Testing, Monticello	Completed
11	Site report, MRY	In progress
12	Site report, Monticello	In progress
13	Final report	In progress



Project Recognition

- DOE kickoff meeting, November 20–21, 2003
- North Dakota Industrial Commission, November 25, 2003

Newspaper/Print

- "EERC awarded funding for mercury research," Basin Today, Mary Klecker, Oct/Nov 2003.
- "Technology bottleneck slows mercury cleanup: Bush Administration cut power plants slack, but too much?" Washington Post, Guy Gugliotta, March 15, 2004.
- "Carbon Removal Technique Tops Mercury Tests," Air Daily, Caroline Gentry, Scientific Journal, March 24, 2004.
- "Large-scale mercury removal testing begins at LOS," Basin Update, March 31, 2004.
- "EERC lands \$7.9 million in mercury research projects," Associated Press. John McFearson. August 26, 2003.
- "EERC lands over \$7.9 million in contracts for mercury control research," *Newswise*. Associated Press. August 27, 2003.
- "EERC gets \$8 million for research: funds could help state's lignite plants remove mercury emissions before EPA regulations set in," Grand Forks Herald. David Dodds. August 28, 2003.
- "UND research center awarded \$7.9 million," Fargo Forum. August 28, 2003.
- "UND research center awarded \$7.9 million," *Jamestown Sun.* August 28, 2003.
- "\$7.9 million given to help research," Bismarck Tribune. August 28, 2003.
- "DOE approves nearly \$10 million for mercury research at lignite-based plants," *Lignite Update*. September 2003.
- "\$5.8 million funds approved for lignite research," *Larimore Leader*. September 4, 2003.
- "\$5.8 million funds approved for lignite research," *Hatton Free Press.* September 4, 2003.
- "\$5.8 million funds approved for lignite research," *Pembina New Era*. September 4, 2003.
- "Delegation announces \$5.8 million for UND energy projects," Medora Billings County Pioneer. September 4, 2003.
- "Delegation announces \$5.8 million for UND energy projects," Beach Golden Valley News. September 4, 2003.
- "EERC lands contract to deal with mercury in coal," Dakota Student. Daryl Sager. September 8, 2003.



Project Recognition (Cont.)

News Releases

- "EERC lands \$7.9 million in contracts for mercury control research," Press Release. EERC.
 Derek Walters. August 26, 2003.
- "Delegation announces \$5.8 million for UND energy projects: Lignite-fired energy plants to take part in research," Press Release. U.S. Senator Earl Pomeroy. August 26, 2003.
- "Conrad announces \$5.8 million for UND energy projects: Lignite-fired energy plants to take part in research," Press Release. U.S. Senator Kent Conrad. August 26, 2003.
- "EERC researchers to receive distinguished service award," Press Release. EERC. Bethany Dennie. November 5, 2003.

TV/Radio Coverage

- "EERC lands \$7.9 million in mercury research projects," 1590 KCNN. August 27, 2003.
- "EERC lands \$7.9 million in mercury research projects," ND Public Radio. August 27, 2003.
- "EERC lands \$7.9 million in mercury research projects," KVLY-TV 11. August 27, 2003.
- "EERC lands \$7.9 million in mercury research projects," WDAZ-TV. August 27, 2003.
- "EERC Mercury Projects." KXJB-TV CBS4, James Degelder. August 28, 2003.
- "EERC Mercury Projects." KVLY-TV 11, James Degelder. August 28, 2003.



Project Deliverables

Deliverable	Description	Status
1	Test plan, MRY	Test Plan completed December 2004
2	Test plan, Monticello	Draft completed March 30, 2005
3	QA/QC plan, MRY	Completed February 2005
4	QA/QC plan, Monticello	Completed
5	Site report, MRY	In progress
6	Site report, Monticello	In progress
7	Final report	In progress



Next Steps and Upcoming Issues

- Upcoming focus areas
 - Complete analysis of samples obtained from the parametric and long-term testing at MRY
 - Characterization of solid samples from MRY testing
 - Complete analysis of data obtained from the parametric and long-term testing at MRY
 - Complete analysis of data obtained from parametric and long-term testing at Monticello
- No current issues of concern

